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POLARIZATION AND SELECTIVE REFLECTION IN THE INFRA-RED SPECTRUM

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY IN CON-
FORMITY WITH THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY.

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SUMMARY.

POLARIZATION AND SELECTIVE REFLECTION IN THE INFRA-RED SPECTRUM

By A. H. PFUND

INTRODUCTION

Object and general survey of the work.—The intimate relationship existing between the refractive index, extinction coefficient, and reflecting power of an absorbing medium was first pointed out by Cauchy in his well-known formulæ for metallic reflection. That these formulæ do actually give a true account of existing conditions has been proved in recent years by Minor,¹ Pflüeger,² Edmunds,³ and others, for conductors as well as for insulators. In deducing his formulæ, Cauchy made the very natural assumption that the intensity of the light, as it penetrated into the medium, fell off according to some exponential law. Now, although this assumption leads to formulæ which are verified by experiment, no insight is obtained into the actual mechanism of reflection, and, in fact, up to the present time a satisfactory theory bearing upon this subject is wanting. It was with the object of collecting data which, it was hoped, might be of some help in solving the problem, that the present work was taken up. For the sake of greater clearness, I wish to give in the following a brief survey of the several investigations carried out.

As indicated by the title, the work naturally falls under two headings:

1. Polarization in the infra-red.
2. Selective reflection in the infra-red.

Heretofore investigators working with polarized radiations in the infra-red have simply assumed that these radiations were polarized, without actually proving them to be so. Therefore the first point to be taken up was to show definitely that these radiations were susceptible of polarization. In the course of the work a new polarizer and analyzer were discovered which are believed to be a decided

¹ *Ann. d. Phys.*, **10**, 581, 1903.

² *Ibid.*, **65**, 214, 1898.

³ *Phys. Rev.*, **18**, 193, 385, 1904.

improvement upon the forms now in use. With these new instruments it was readily proved, as far as the experiment could be carried (i. e., up to $13\ \mu$), that infra-red radiations can be polarized by reflection.

One of the distinguishing properties of a metal is its ability to convert plane into elliptically polarized light by reflection. It was thought of interest to investigate whether an insulator reflecting metallically in the infra-red would also have this property. The substance chosen was Iceland spar, and it was shown conclusively that the conversion of plane into elliptically polarized light does take place—as might have been expected.

Originally it was intended to determine the refraction and extinction curves for Iceland spar within the region of metallic reflection by a katoptric method which involved a determination of the constants of elliptically polarized light. The method employed was the well-known Brewster's double mirror method as used by Quincke,¹ Pflueger (*loc. cit.*), and others. It was shown by the use of silver mirrors that such measurements can easily be carried out into the infra-red. Unfortunately, however, in the case of Iceland spar the amount of energy reaching the radiometer was too small to make accurate measurements possible.

The object of the work on selective reflection was the following:

According to modern conceptions, selective reflection from insulators is occasioned by particles with definite free periods which are capable of vibrating in resonance with certain incident radiations. As the phenomenon is looked upon as taking place entirely within the molecule, it was thought of interest to determine, first, whether the selective reflection of a substance was dependent on its physical state, and, secondly, whether the mechanism giving rise to this selective reflection was localized within some definite portion of the molecule. As to the first point, the selective reflection of a salt was studied, both when the salt was solid and when molten; and as to the second point, an investigation was carried out on the selective reflection of a number of salts having a certain radical in common.

Having found that a molten salt is capable of reflecting selectively, a number of other molten salts and liquids were investigated for

¹ *Pogg. Ann.*, Jubelband, 336, 1874.

similar effects. In the case of sulphuric acid some very remarkable changes in the reflection-curve were found as the acid was diluted. Each of these subjects in turn will be discussed in detail.

DESCRIPTION OF APPARATUS

Radiometer-spectrometer.—The general arrangement of the apparatus is shown in the following diagram (Fig. 1):

Radiations coming from a Nernst glower (N) placed in front of the slit (S_1) were rendered parallel by the concave mirror (M_1),

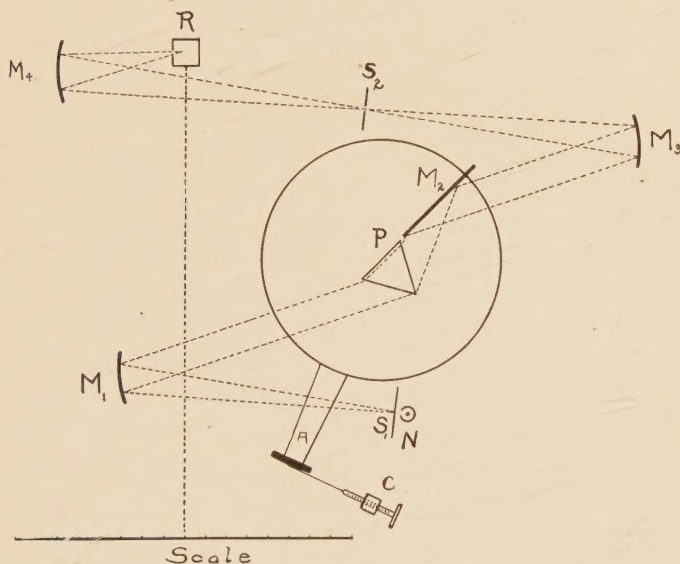


FIG. 1

and then passed through the Wadsworth mirror and prism arrangement (PM_2). The mirror (M_3) brought the spectrum of the source to a focus on the second slit (S_2). Thus, by a rotation of the prism and mirror system (PM_2) mounted on the spectrometer, it was possible to cause the entire spectrum to pass over the slit S_2 , and in this manner any desired portion could be brought to a focus on one of the blackened vanes of the radiometer R . The slits S_1 and S_2 were usually opened to a width of 0.5 mm.

As mentioned, the source of radiation was a Nernst glower inclosed in a brass cylinder which had but one narrow opening along its

side. In this manner the disturbing effects of air currents were removed, as shown by actual tests of the constancy of the radiation of the glower. The concave mirrors (M_1) and (M_3) had a radius of curvature of 52 cm, while the mirror M_4 , which concentrated the radiations on the radiometer vane, had a radius of curvature of only 26 cm. The rock-salt prism (P) was about 5 cm on an edge and had a refracting angle of $60^\circ 10' 6''$. The calibration was carried out in the usual manner of calculating from the known dispersion-curve of rock salt, the deviations corresponding to definite wavelengths. To check the results thus obtained, the position of the emission bands of CO_2 from a Bunsen burner ($2.70\ \mu$ and $4.40\ \mu$), and also the position of the bands of metallic reflection from quartz ($8.49\ \mu$ and $9.03\ \mu$)¹ and from Iceland spar ($6.69\ \mu$ and $11.41\ \mu$), were observed, and were found to lie exactly on the curve.

Concerning the spectrometer the only point worth mentioning is that the rotation of the prism and mirror system, which was mounted on the spectrometer table, was measured by means of a micrometer (c) connected with the projecting arm (A) through a piece of steel tape. The length of the arm was so chosen that one division on the divided barrel of the micrometer corresponded to 6 seconds of arc.

The radiometer was of the usual Nichols type and was supplied with a rock-salt window. The sensibility of the instrument could easily be varied by changing the length of the quartz fiber which was partly wound up on a miniature reel arrangement. In the polarization experiments the sensibility was such that a meter-candle gave rise to a deflection of about 1000 mm, while in the later reflection experiments the sensibility was reduced to six-tenths of this value. With the exception of the rock-salt window and the minute concave mirrors about to be described, the radiometer was identical with the one employed by J. T. Porter² and described by him.

Throughout the course of the entire investigation this radiometer-spectrometer remained unmodified, all of the special apparatus being brought out in front of the slit S_1 .

Minute concave mirrors.—Undoubtedly the easiest way of deter-

¹ These values, obtained by Rosenthal (*Ann. der. Phys.*, **68**, 783, 1899), are probably the most accurate known.

² *Astrophysical Journal*, **22**, 229, 1905.

mining the deflection of a radiometer is to observe the motion of the image of an incandescent lamp filament projected on a ground glass scale by means of a small concave mirror. Heretofore this method has not been used, for the reason that small concave mirrors weighing a milligram or two have not been obtainable. It occurred to me that they might very easily be made in the following manner.

A small concave mirror or good spectacle lens of about 1 m radius of curvature is heavily silvered and polished on its concave side, and is then cut up into strips about 4 mm wide. If, now, one of these strips be struck a smart tap on its edge by means of a flat file, small scales of glass bearing silver on one side can be caused to fly off. These scales are, of course, the concave mirrors in question. With a little practice it is easy to produce mirrors of this kind varying from 7 or 8 mm in diameter down to infinitesimal dimensions. These mirrors are found to retain their figure well, and to give images of surprising sharpness and brilliancy.

In making such small mirrors care must be taken to select a concave mirror of good figure, and an easy way to carry out a test is to diaphragm off all of the mirror but an area about 2 mm square, and then to examine the image produced. If it be necessary to use these mirrors in the open air, where silver will tarnish, it would be advisable to platinize the reflecting surface by cathode discharge.

POLARIZATION IN THE INFRA-RED

Reflection from glass and selenium.—Ultra-violet, visible, and short infra-red rays may readily be polarized by means of some such device as a Nicol or Rochon prism. However, beyond 2.5μ in the infra-red spectrum this method fails on account of the opacity of the doubly refracting substance, Iceland spar, used in the construction of the above-named polarizers. Probably the most convenient method of producing polarized radiations in the regions of great wave-lengths is that involving reflection at the polarizing angle from some transparent substance. The conditions which such a substance must fulfil are:

1. It must have a fairly high reflecting power.
2. Its polarizing angle must be practically constant for different wave-lengths.

3. It must polarize very completely.

The obvious manner of attacking the problem is to make a study of the reflection-curves of various substances which appear to give promise of fulfilling the above-mentioned conditions. The apparatus used in carrying out such measurements is shown in the following diagram (Fig. 2).

Radiations from the Nernst glower at N were reflected at an angle of incidence of 10° from the two mirrors (M_2) and (M_3), and were finally brought to a focus on the slit S_1 of the spectroscope already described. The mirror whose reflecting power was to be determined

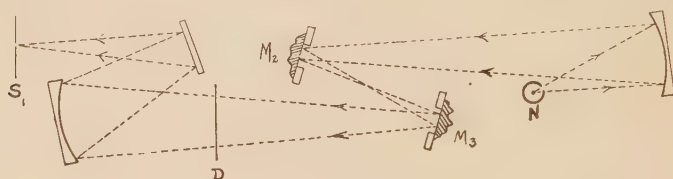


FIG. 2

was held in position at (M_3) by being pressed against a brass plate into which a hole had been cut. Any desired mirror could be placed behind the opening of a similar brass plate at (M_2). In order to keep the deflections on the scale, a diaphragm was placed at D which could be made to cut down the vertical aperture of the beam. Measurements of reflecting power were obtained in the following manner. The mirror to be tested was placed in position at M_3 , and the radiometer deflection was noted; then a silver mirror was made to replace the former, and again the deflection was noted. The ratio of the latter deflection to the former gave the reflecting power of the substance for the wave-length corresponding to a given spectrometer setting.

Considerable time was lost in trying to adjust the two mirrors (i. e., the one of silver and the other of the material under investigation) upon a rotating table which could be made to move between stops. Due to the fact that the replacement of one mirror by another was not absolutely exact, very discordant results were obtained. Consequently this method was abandoned, and the one already described was used—thereby making the replacement of one mirror by another exact beyond a question. As might be expected, very concordant results were obtained.

In looking over some unpublished results on the reflecting power of amorphous selenium, it appeared to me that the reflecting power of this substance gave promise of becoming constant for the longer wave-lengths, and it was decided to make some exact measurements. Furthermore, since glass has been repeatedly used in the infra-red as a polarizer, it was thought worthy of interest to determine in what regions of the spectrum such a procedure would be permissible. The results as plotted in the following curves (Fig. 3) speak for themselves.

That glass would be unfit to act as a polarizer throughout the entire spectrum might have been predicted from a knowledge of

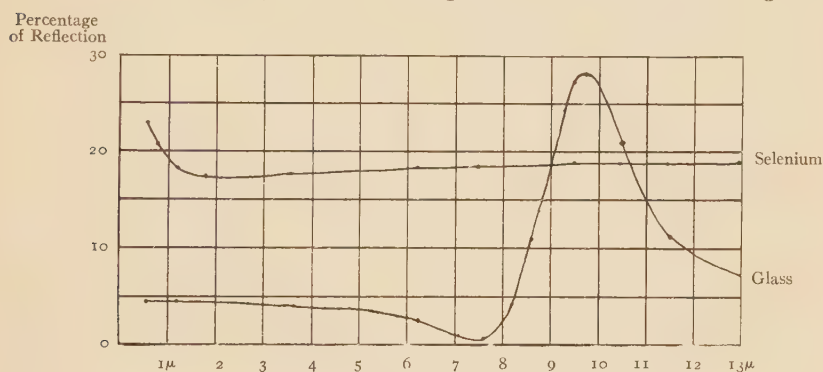


FIG. 3.—Glass and Selenium.

the fact that it contains SiO_2 , which gives rise to the bands of metallic reflection of quartz. In the case of selenium it will be observed that the reflecting power is not only very high, but also very constant; hence this substance is eminently adapted to serve as a polarizer.

Since in experiments with polarized light two reflections are necessary, one from the polarizer and one from the analyzer, the maximum attainable energy after two reflections is to the incident energy as $r^2:1$, where r is the reflecting power of the polarizing medium. This statement would be rigorously true if the incident energy were already polarized in the plane of incidence. Taking into account the fact that this is not the case—i. e., considering the fact that the incident radiations are unpolarized—calculations have been made upon the basis of Fresnel's formulæ to show how great

the gain in energy is when selenium is used as polarizer and analyzer in place of other substances.

Refractive Index of Substance	Fraction Refl. from Polarizer	Fraction Refl. from Analyzer	Ratio of Emergent to Incident Energy	Gain in Using Selenium
2.565 (selenium).....	0.27	0.54	0.146	
1.60.....	.095	.19	.018	8.1 times
1.50 (rock-salt).....	.0745	.149	.011	13.3 "
1.40 (fluorite).....	.0515	.103	.0053	27.6 "
1.30 (fluorite).....	.0375	.075	.0028	52.0 "

Since selenium is comparatively transparent in the infra-red, it will be permissible to apply Fresnel's reflection formulæ and calculate the refractive index (n):

$$n = \frac{1 + \sqrt{r}}{1 - \sqrt{r}}.$$

Near $13\ \mu$, where the reflection-curve becomes flat, $r=19$ per cent., and the refractive index as calculated is $n=2.565$. Now, according to Maxwell's equations the relation $n^2=\epsilon$ (where ϵ is the dielectric constant) is fulfilled if the measurements be made sufficiently far removed from the region of absorption bands. Recently Schmidt¹ has found that for amorphous selenium $\epsilon=6.60$, while from the foregoing measurements we have $\epsilon=n^2=6.58$. This shows that the Maxwellian relation is already fulfilled, and it seems only reasonable to suppose that the reflecting power, and hence the polarizing angle, will remain constant throughout the remainder of the infra-red spectrum.

The selenium mirrors used in the experiments about to be described were prepared in the following manner. Some pure selenium was melted down in a porcelain crucible and was poured on a plate of hot glass; a second plate of hot glass was then quickly pressed down upon the pool of molten selenium, and the whole was laid on an iron plate to cool. The layer of selenium, after being pressed out, was usually about 1 mm in thickness. Heretofore considerable difficulty was experienced in getting the second plate to come off. I have found, however, that this can be accomplished very easily

¹ *Ann. d. Phys.*, 2, 114, 1903.

if the second plate be made considerably longer than the first, thereby making it possible to bend it slightly and thus cause it to tear itself away from the selenium. Very beautiful mirrors may be obtained in this manner. Those actually used were of oval shape, about 10 cm long and 5 cm wide, and had a figure as perfect as that of the glass plate which had covered them.

By means of such mirrors as these a polarizer of the following form was constructed (Fig. 4):

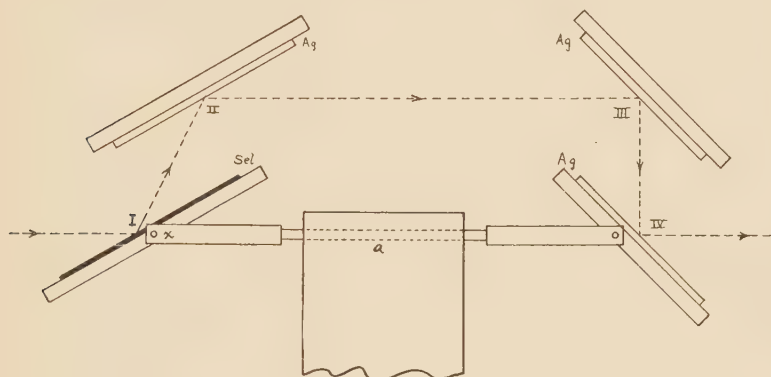


FIG. 4

Selenium polarizer and analyzer.—The selenium mirror (I) and the silver mirror (2) were adjusted parallel, and then rigidly connected with one another, so that a rotation about the axis (x), changing the angle of incidence, would not change the direction of the emergent beam. The two other silver mirrors (3) and (4) were also adjusted parallel to one another, and the entire system could be rotated about the axis a (the axis a being perpendicular to the axis x). It is easy to see that in an apparatus of this kind the incident and emergent beams lie along the same straight line, and a rotation about the axis a will not affect the direction of the emergent beam. Therefore, if this beam be concentrated upon the slit of a spectrometer, it will remain there in spite of the rotation of the mirror system.

In the actual experiments the instrument just described was used as the analyzer, while the polarizer was made to consist of the mirrors (I) and (2) alone. In order to measure the rotations of the system of mirrors, small protractors graduated to $30'$ were fas-

tened to the axis a . By means of a telescope tenths could be easily estimated, thus making it possible to read to $3'$ of arc.

Complete polarization of infra-red radiations.—As was mentioned in the beginning, the first question taken up was whether this apparatus would actually polarize infra-red radiations. The manner in which the experiment was carried out is shown in the accompanying diagram (Fig. 5). The rays from the Nernst glower (N), after being rendered parallel by the concave mirror M , were polarized at P , and then analyzed at A . The concave mirror (M_2) focused

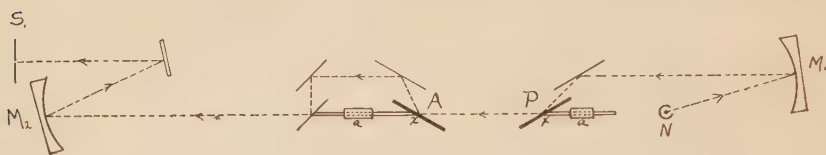


FIG. 5

the image of the Nernst glower on the slit S_1 of the spectrometer already described. Having roughly adjusted the selenium mirrors of the polarizer and analyzer in the position of maximum polarization, they were "crossed," and the position of least reflection was determined by successive rotations of the systems about the axes x and a . This position could be found very easily, and the fact was established that variations in the angle of incidence of a degree or two did not markedly influence the results. Deflections of the radiometer were observed up to $13\ \mu$ corresponding to the condition of parallel and crossed polarizer and analyzer. Results of the following character were obtained throughout this entire range of wave-lengths:

Relative Position of Polarizer and Analyzer	Radiometer Deflection
Parallel	$> 1000\ \text{mm}$
Crossed	$< 1\ \text{mm}$

This shows, then, that the radiations are polarized to a very high degree. Of course, no claim is made to complete polarization, as it is found that, if the incident energy be increased very greatly, a small deflection of a few divisions is obtained. All things taken into consideration, however, selenium is found to fulfil the conditions imposed upon it as a polarizer very well indeed.

Elliptical polarization from Iceland spar in the region of metallic

reflection.—In order to determine whether a non-metallic substance in its region of metallic reflection behaves as a metal toward polarized light, a parallel beam of radiations (Fig. 6) from a Nernst glower (N) polarized in an azimuth of 45° at P was caused to be reflected from a surface of Iceland spar (I) (polished on one of its

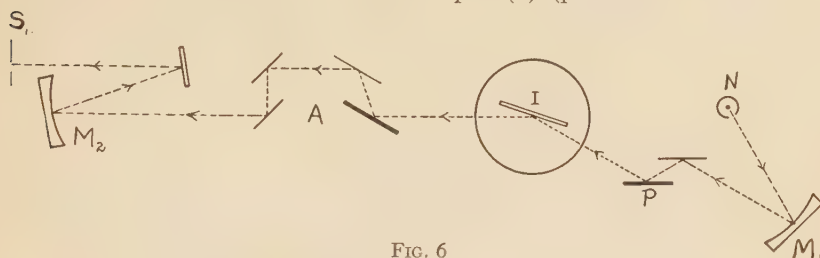


FIG. 6

cleavage planes) at an angle of incidence of 65° . After passing through the analyzer (A), these radiations eventually reached the slit (S_1) of the spectrometer. For a given setting of the spectrometer, radiometer reflections were observed corresponding to the two positions of the analyzer giving maximum and minimum energy. The readings here recorded are for $\lambda = 4 \mu$, where Iceland spar reflects vitreously, and for $\lambda = 6.70 \mu$, where it reflects metallicly.

	Maximum Deflection	Minimum Deflection	Ellipticity (Ratio of Axes)
4.0μ	501 div.	0 div.	10:0
6.7μ	90 "	55 "	10:6

These results show conclusively that Iceland spar transforms plane into elliptically polarized light within the region of metallic reflection.

On account of the difficulty of preparing plates of Iceland spar or quartz sufficiently thin to make transmission and absorption measurements possible within the regions of metallic reflection, it was thought feasible to make these measurements by an indirect, katoptric method. As stated earlier in the paper, the amount of energy reaching the radiometer was found insufficient to make such determinations possible. When it is considered that the radiations suffered fifteen reflections before reaching the radiometer, it is not surprising that the available amount of energy was found too small.

However, the work of Pflueger (*loc. cit.*) and Nichols¹ on insulators, and of Hagen and Rubens² and Minor on metals, has unquestionably established the fact that strong absorption and metallic reflection go together. In view of the fact that any explanation of metallic reflection involving the conception of resonance is not applicable to metals, one is led to suspect that metallic reflection, wherever found, is, in all probability, to be attributed to strong absorption alone.

SELECTIVE REFLECTION IN THE INFRA-RED

Reflection from solid and molten salt.—In order to determine the selective reflection of various substances, such investigators as Rubens and Nichols,³ Aschkinass,⁴ and Porter (*loc. cit.*) made use of the method of multiple reflections, commonly known as the method of "Reststrahlen." On account of the weak reflecting power of most of the substances investigated in the present work, it was decided not to use the above method, but rather to make direct determinations of the reflecting power. In the case of solids the same method was used as that described in the chapter dealing with the reflection from selenium, while in the case of liquids the method used involved the reflection of energy from the free liquid surface.

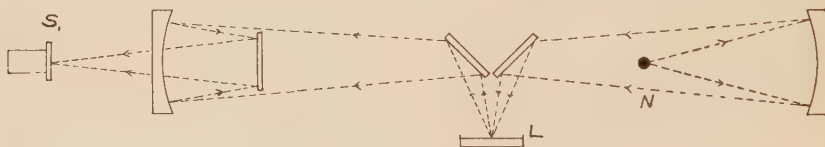


FIG. 7

The general arrangement of apparatus is shown in elevation in the diagram (Fig. 7):

Radiations from the Nernst glower *N* were first brought to a focus on the surface of the liquid at *L*, and finally on the slit *S*, of the spectrometer. Measurements were obtained in the following manner: With the liquid surface in a fixed position a complete series of readings was taken throughout the entire spectrum; then the liquid surface was replaced by one of silver, and a similar series

¹ *Sitzungsberichte der Kgl. Preuss. Akad. der Wissenschaften*, 44, 1, 1896.

² *Ann. d. Phys.*, 8, 1, 1902.

³ *Ibid.*, 60, 418, 430, 1897.

⁴ *Ibid.*, 65, 241, 1898.

was taken. By proceeding in this manner it was possible to make corrections for a rising or falling energy-curve of the source. The principal reason for adopting this method of procedure in preference to the one used before was that certain liquids, especially the molten salts, had a most annoying tendency to form "surface skins," and it was only by stirring the molten mass vigorously, and then taking the readings in the shortest time possible, that concordant readings could be obtained. It might be added that the radiations sent out by the Nernst glower were of an amply sufficient constancy to make

α , Reflecting
Power

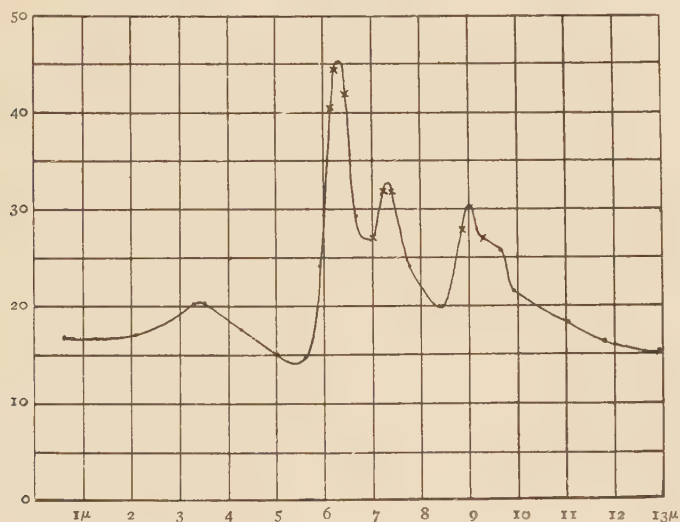


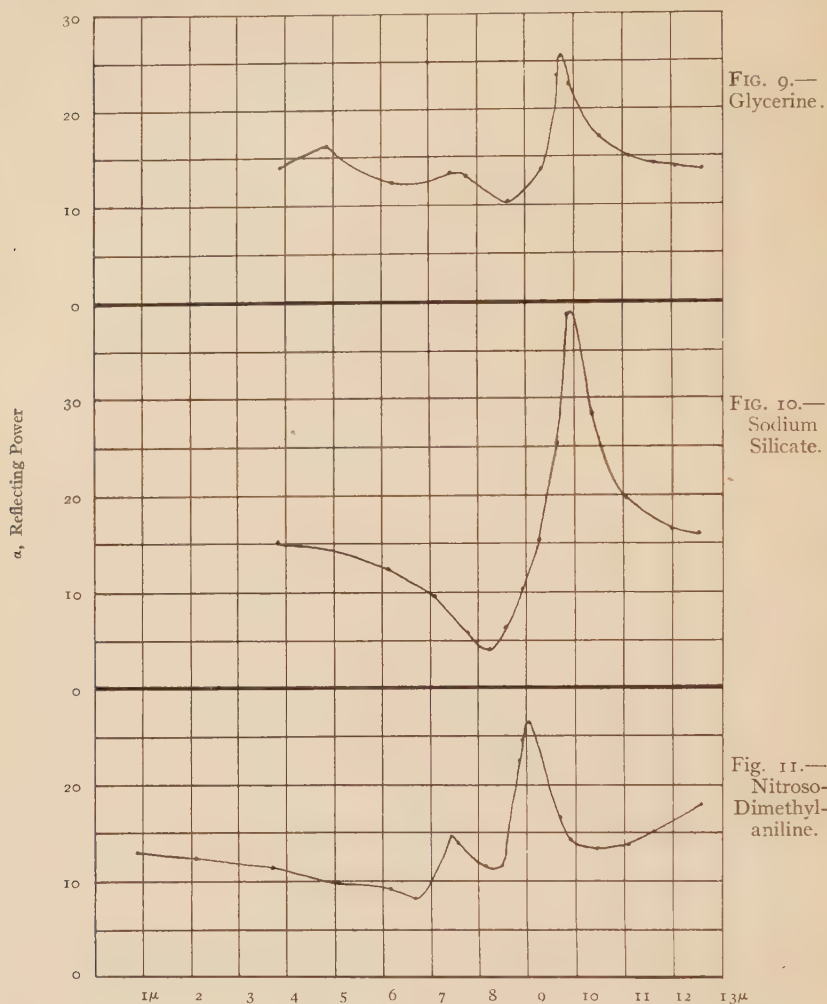
FIG. 8.—Sodium-Potassium Tartrate.

such a procedure allowable. On each of the curves plotted it is indicated whether the ordinates are proportional or equal to the reflecting power.

The intensity of reflection from most of the liquids examined, even at the maxima, lies under 15 per cent. The only exception is sulphuric acid, which at its highest maximum reflects 20.8 per cent.

The first point to be taken up was to show that, so long as the molecule as a whole remains unaltered and no changes take place in the nature of the surrounding medium, the position of the bands of metallic reflection will remain the same. The substance chosen

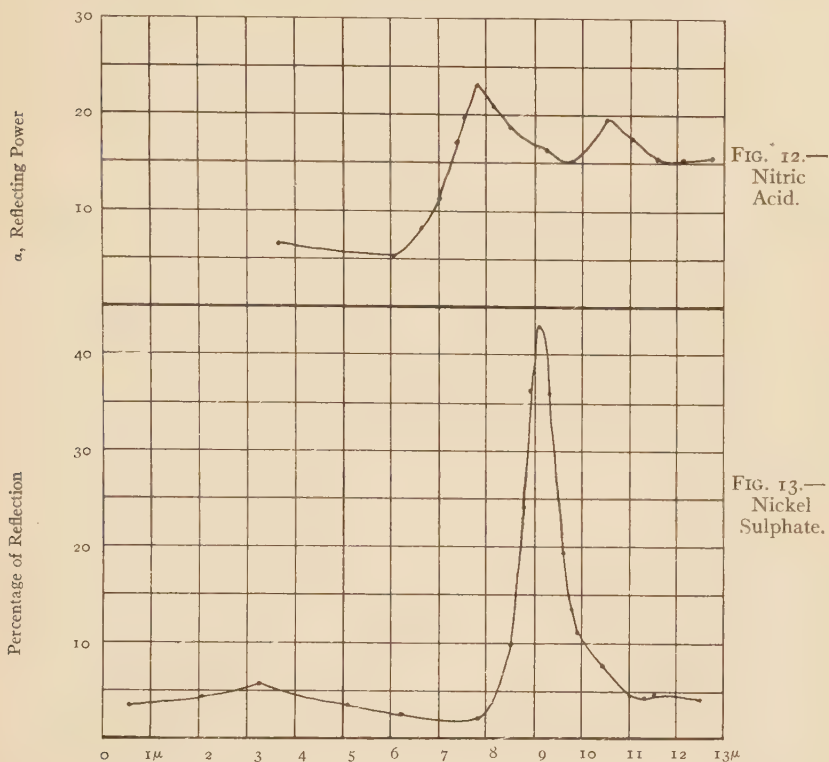
to show this was sodium potassium tartrate. A reflection-curve was obtained from a polished crystal, and then an attempt was made to obtain a similar curve for the molten salt. Unfortunately,



however, it was not possible to obtain a complete curve of this kind, on account of the rapid formation of a surface skin, and in consequence I had to content myself with a determination of the positions of the maxima, which were very marked. This was done by setting

the spectrometer approximately in the position of a band, then removing the surface skin and making an accurate setting before a new skin had time to form. The readings thus obtained are indicated by crosses on Fig. 8, and show that the position of the bands remain unaltered.

Reflection from liquids.—In view of the fact that molten sodium potassium tartrate was found to possess bands of metallic reflection,



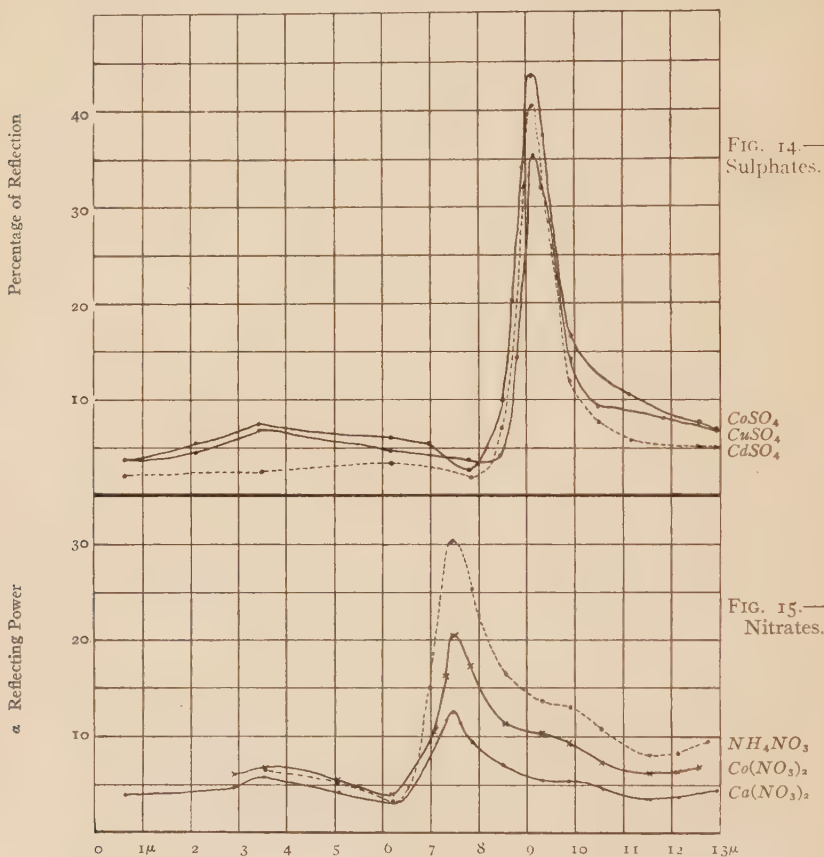
it was deemed of interest to investigate other molten salts and liquids for similar effects. The accompanying curves (Figs. 9–12, 14, and 15) for glycerin, liquid sodium silicate, molten nitroso-dimethyl-aniline, nitrates of calcium, cobalt, magnesium and ammonium, nitric acid, and sulphuric acid show in a most striking manner that selective reflection is by no means confined to solids.[†] It might be added

[†] No marked bands of selective reflection were found for wave-lengths shorter than 3 μ .

that no such marked maxima were obtained when water, alcohol, molten caustic potash, phosphoric acid, acetic acid, and hydrochloric acid were tried.

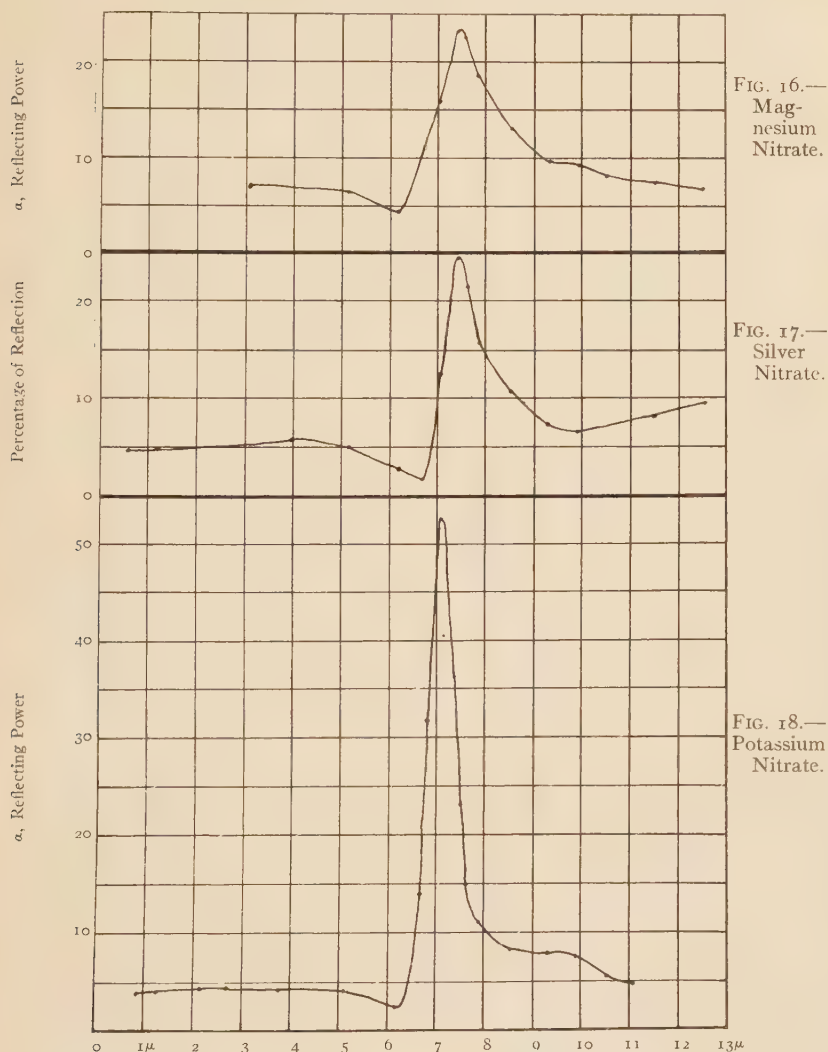
Localization of mechanism of selective reflection within molecule.—

Upon looking over the results obtained, it became very evident that



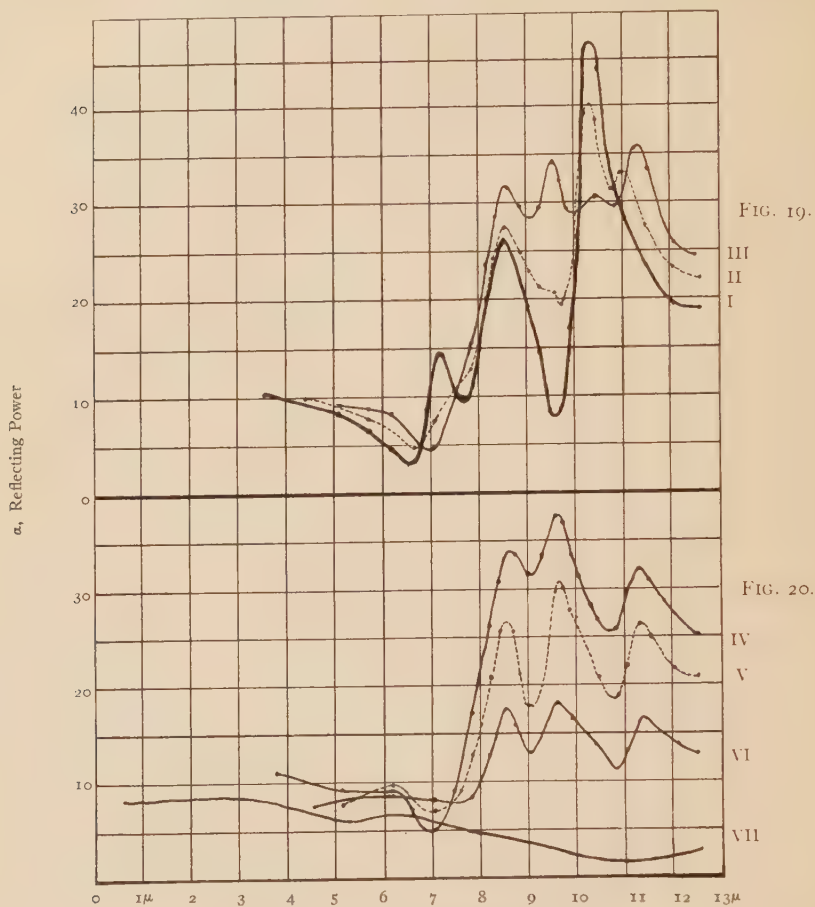
salts of the same acid had curves whose principal maxima were situated in the same region of the spectrum, and it was decided to investigate this point more fully. Consequently, the selective reflection of the following substances was investigated: sulphates of copper, nickel, cadmium, iron, sodium, potassium, and cobalt; also the nitrates of silver and potassium in addition to those of calcium, ammonium, magnesium, and cobalt already investigated. Whenever

crystals were obtained whose surfaces were of sufficient size and perfection, the absolute values of the reflecting powers were determined. Where this was not the case, it was possible to obtain only



relative values of the reflecting power. Finally, in the case of the sulphates of sodium, potassium, and iron only a determination of the positions of the maxima was made.

An inspection of the following curves, as for example those of the sulphates (curves 13 and 14), cannot fail to impress one with the fact that the maximum near 9.05μ is present under all circumstances, no matter what the nature of the metal in the molecule may



FIGS. 19 and 20.—Fuming Sulphuric Acid.

be. Again in the case of the nitrates, it is equally evident that the strong maximum near 7.40μ appears in all cases. Attention must, however, be called to the fact that the position of the maxima for the salts of a given acid are not identically the same as will be observed if the curves for silver nitrate and potassium nitrate (Figs. 17 and

18) are compared; nor do the maxima of sulphuric and nitric acid coincide with those of the sulphates and nitrates respectively. These points will be discussed later on. However all this may be, one cannot help but acknowledge that the similarity of the curves, especially of those shown in Figs. 14 and 15, is too striking to be without significance. Since every salt of a given acid thus far studied shows a maximum in approximately the same region of the spectrum, in spite of marked changes in the nature of the metal, one is strongly tempted to localize the mechanism giving rise to this maximum in the acid radical of the molecule, i. e., that portion of the molecule which in solution becomes the negative ion.

Reflection from fuming sulphuric acid at various dilutions.—In order to reassure myself of the correctness of the results which had thus far been obtained, a second series of measurements was carried out for all of the substances studied. All of the results were verified, with the exception of those for sulphuric acid, which were totally different from the first. As was later found out, this was due to the fact that the wrong sulphuric acid bottle (containing weak acid) had been used. On account of the striking difference in the two curves, it was decided to make a systematic investigation of the changes in the forms of the curves corresponding to different degrees of dilution of the acid. The curves Figs. 19 and 20 represent the results obtained.

Curve I is for undiluted fuming sulphuric acid of density 1.87

" II " " 12 parts of this acid and 1 part of water

" III " " 12 " " " " " 2.4 " " "

" IV " " 3 " " " " " 1 " " "

" V " " 1 part " " " " " 1 " " "

" VI " " 1 " " " " " 3 parts " "

" VII " " pure water (distilled).

These proportions of acid to water are given in terms of volumes.

In curve I three distinct maxima are discernible—at $7.20\ \mu$, $8.65\ \mu$, and $10.30\ \mu$; and also three minima—at $6.62\ \mu$, $7.73\ \mu$, and $9.64\ \mu$. Curves II and III, which represent intermediate stages, show that the maximum at $10.30\ \mu$ is rapidly disappearing; the minimum at $9.46\ \mu$ is being filled in; the maximum at $8.65\ \mu$ remains, while the maximum at $7.20\ \mu$ also disappears. In addition to these

changes, other maxima are coming in, whose positions from curves IV and VI are seen to be at $9.60\ \mu$ and $\overset{11.40}{7.46}\ \mu$. As will be observed, these maxima are distinctly new and are not the old ones displaced to another position. Furthermore, it is evident from curve VII that water superimposes no peculiarities of its own on the curves for sulphuric acid.

I have tried to interpret these results in the following manner.

It is generally conceded that in sulphuric acid of the greatest strength used in these experiments there is a large excess of undissociated H_2SO_4 molecules. By an addition of water, these molecules are first broken down into $\overset{+}{H} \overset{-}{HSO}_4$ ions, and finally into $\overset{+}{H} \overset{+}{H} \overset{-}{SO}_4$ ions—the complete change to the latter form taking place only at infinite dilution. Considering the fact that these changes in the molecules and ions are accompanied by marked changes in the reflection-curves, it seems only reasonable to suppose that those maxima, which are at first present and then disappear with increasing dilution, are due to molecules or ions (or possibly both) which also disappear with increasing dilution. Similarly, the new maxima which appear are supposed to be due to new ions which are formed in consequence of increasing dilution. It would, indeed, be premature to attempt to attribute with definiteness certain reflection maxima to certain molecules or ions; for the state of our knowledge as to the condition of affairs existing in solutions is as yet too incomplete. In the present case, for example, we have fuming sulphuric acid (which is a solution of SO_3 in H_2SO_4) and water. Not only is it possible to have a large number of different kinds of ions, but in addition we may have a large number of complexes or hydrates which the molecules of the acid might form with those of the water. From this it will be seen that much work remains to be done to clear up the subject.

But let us return once more to the work on the sulphates and nitrates. As already pointed out, this work has made it seem probable that the mechanism giving rise to certain strong maxima of reflection is localized within the acid radical. Now, this conclusion is quite in accord with the results of some calculations which Drude¹

¹ *Annalen der Physik*, 14, 677, 1904.

has recently carried out. In these it is shown that the particle which, in consequence of its sympathetic vibrations, gives rise to the ultra-violet absorption band has a charge and a mass identical with that of the corpuscle, while the particle giving rise to the infra-red absorption band has a mass of the order of magnitude of the molecule itself. Since it is a large portion of the molecule which is looked upon as being thrown into vibration, it does not seem difficult to account for the fact that the positions of the reflexion maxima for the salts of the same acid are not the same. There is but little doubt in my mind that the positions would be the same if the acid radicals could execute their vibrations independently of other particles surrounding them—a condition approached at infinite dilution. In the cases actually studied the freedom of motion of the acid radical depended not only on the closeness of the bond between it and the metal ion, but also upon molecules of water clustering around it. It does not seem unreasonable, therefore, to suppose that these influences might affect the period of vibration of the acid radical, and hence the position of the reflection maximum.

The following table gives a list of the substances studied, together with the positions of the principal maxima of reflection:

Substance	Formula	Position of Reflection Maxima			Remarks
<i>Na-K</i> tartarate	$C_8H_4KNaO_6 \cdot 4H_2O$	6.35	7.35	9.05 μ	Solid crystal
Magnesium nitrate . .	$Mg(NO_3)_2 \cdot 6H_2O$	7.45			Molten
Cobalt nitrate	$Co(NO_3)_2 \cdot 6H_2O$	7.45			"
Ammonium nitrate . .	NH_4NO_3	7.45			"
Calcium nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	7.45			"
Silver nitrate	$AgNO_3$	7.45			Solid crystal
Potassium nitrate . .	KNO_3	7.05			" "
Nickel sulphate	$NiSO_4 \cdot 7H_2O$	9.05			" "
Cobalt sulphate	$CoSO_4 \cdot 7H_2O$	9.05			" "
Copper sulphate	$CuSO_4 \cdot 5H_2O$	9.15			" "
Cadmium sulphate . . .	$CdSO_4 \cdot 4H_2O$	9.10			" "
Ferric sulphate	$Fe_2(SO_4)_3 \cdot 9H_2O$	9.05			" "
Sodium sulphate	$Na_2SO_4 \cdot 10H_2O$	9.02			" "
Potassium sulphate . .	K_2SO_4	8.85			" "
Fuming sulphuric . . .	H_2SO_4 and SO_3	7.20	8.60	10.35 μ	Naturally fluid
Acid and water	in H_2O	8.60	9.60	11.35	" "
Nitric acid	HNO_3	7.85	10.55		" "
Glycerine	$C_3H_8O_3$	4.80	9.70		" "
<i>Na</i> -Silicate	Na_2SiO_3	9.95			" "
Nitroso-dimethyl aniline	$(CH_3)_2NC_6H_4NO$	7.40	9.00		Molten

SUMMARY •

The results of this investigation may be summed up briefly as follows:

1. The reflecting power of amorphous selenium has been studied out to $13\ \mu$. In consequence of the high and constant reflecting power of this substance, it was used in the construction of a polarizer and analyzer, adapted for work throughout the entire infra-red spectrum.

2. It was shown that infra-red radiations are capable of being polarized out to a wave-length of $13\ \mu$, which was as far as the experiments could be carried.

3. It was shown that the non-metallic substance, Iceland spar, in its region of metallic reflection transforms plane into elliptically polarized light by reflection. This shows that, so far as its behavior toward plane polarized light is concerned, there is nothing to distinguish a non-metal from a metal.

4. Upon finding that the positions of the bands of selective reflection from a solid salt (*Na-K* tartrate) remain unchanged when the salt is molten, it is concluded that the mechanism giving rise to these bands is not affected by the freedom of motion of the molecule as a whole, and is therefore in all probability localized within the molecule itself.

5. By examining numerous liquids, it was found that these, as well as the solids, possess bands of selective reflection in the infra-red.

6. In the case of fuming sulphuric acid it was found that marked changes in the reflection-curves appeared when the acid was diluted. It was concluded that these changes were due to the breaking-down of certain compounds in solution and the consequent formation of new ones.

7. From the marked similarity in appearance and position of reflection maxima of the salts of a given acid (nitrates and sulphates) it was concluded that the mechanism giving rise to these maxima was localized within the acid radical.

Most of the substances used in this work were obtained through the kindness of Professor Harry C. Jones, of the Chemical Labora-

tory, and it is with pleasure that I acknowledge my indebtedness to him.

The present investigation has been carried out during the past year under the direction of Professor Ames, whom I wish to thank most heartily for his many valuable suggestions and his never-failing interest in the progress of the work.

JOHNS HOPKINS UNIVERSITY,

April, 1906.

BIOGRAPHY

August Herman Pfund was born December 28, 1879, at Madison, Wisconsin. He received his early training in the public schools of that city and in the fall of the year 1897 entered the University of Wisconsin, from which he graduated after four years with the degree of B.S. He devoted the next two years (1901-3) to graduate work at that institution.

In the fall of 1903 he entered the Johns Hopkins University as graduate student and also as Carnegie Assistant to Professor R. W. Wood—a position which he held up to the spring of 1905, when he was elected regular Fellow in Physics for the year 1905-6.

While at the Johns Hopkins University he followed the courses of Professors Ames, Wood, and Whitehead (in Physics), Jones (in Physical Chemistry), and Cohen (in Mathematics).

